Title: **Characterization of Liquid Products from All-Slurry-Mode Direct Liquefaction**

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BACKGROUND

The state-of-the-art coal liquefaction technology in the U.S. can now produce, at historically low costs, premium distillate products that can be co-refined with petroleum in existing refineries. The value of modern direct liquefaction liquid products can be determined using refinery linear programming (LP) models, such as the Process Industry Modeling System (PIMS) developed by Bechtel Corporation. To perform refinery LP studies, crude assay data of coal liquids are needed. Supported by the U.S. Department of Energy (U.S. DOE) Federal Energy Technology Center (FETC), CONSOL Inc., and Burns and Roe Services Corporation have coordinated the characterization of nine representative direct coal liquefaction products generated from Wilsonville operation and Hydrocarbon Technologies, Inc. (HTI) facilities.

Two all slurry-mode coal liquefaction liquid products were recently analyzed by Inchcape Testing Services (ITS).[1] The coal liquid samples were collected from HTI's Run PB-03, a continuous bench-scale operation with Black Thunder mine subbituminous coal as feed and dispersed catalysts in both reactor stages. One sample, designated as PB3a, was produced while a fixed-bed, in-line hydrotreater unit (HTU) was on-stream and the other, PB3b, was generated while the HTU was by-passed. This is the first time that all-slurry-mode liquefaction products were analyzed using ASTM procedures and methods and the first time that the effect of the HTU on product quality could be determined.

This paper summarizes the two coal liquid assays on the all-slurry-mode PB-03 coal liquids and compares them with an assay conducted by Conoco Inc.[2] on an ebullated-bed reactor product collected from HTI's Run POC-2 (a Proof-of-Concept operation also using Black Thunder Mine coal and employing an HTU). The comparison provides information on the effect of catalyst types and reactor configurations. Operating conditions of Runs PB-03 and POC-2 from which samples were collected are listed in Table 1.

DISTILLATION AND YIELD STRUCTURE (MILD HYDROCRACKING IN HTU)

Figure 1 is the simulated true-boiling-point (TBP) curves of coal liquids PB3a and b, with POC-2 for comparison. Clearly, PB3a, which was processed in the in-line hydrotreater, is much lighter than PB3b, which did not pass through the HTU. A comparison of the yield structure of the two liquids follows:

	PB3a	PB3b
IBP, °C	42.3	69.7
Yield, vol %		
Light naphtha (IBP-82 °C)	5.3	2.0
Medium naphtha (82-177 °C)	32.7	22.7
Heavy naphtha (177-204 °C)	10.7	9.3
Light distillate (204-288 °C)	29.7	33.7
Heavy distillate (288-350 °C)	16.5	19.8
EP, °C	420.9	485.5

The in-line hydrotreatment decreased the initial boiling point (IBP) and end point (EP) of the coal liquid by 28 and 65 °C, respectively, and increased the yields of light, medium, and heavy naphthas by 3.3, 10, and 1.4 vol % (absolute), respectively. The total yield of <350 °C fractions increased by 7.3 vol % (abs.). In addition to its highly efficient hydrogenation activity, which is discussed in the following sections, the in-line hydrotreater also performed mild hydrocracking; it converted approximately 20 vol % of the >204 °C material into naphtha range products.

Figure 1 also shows that the distillation curve of the POC-2 coal liquid (also produced with Black Thunder coal and an in-line HTU, but with two-stage ebullated-bed reactors) is close to that of the PB3a liquid; demonstrating the similarity in vaporization characteristics of coal liquids produced via two-stage liquefaction with in-line hydrotreating.

PROPERTIES OF PB-03 LIQUID PRODUCTS

For the sake of simplification, only the primary properties of the PB3a and PB3b liquids are tabulated (Tables 2 and 3). Additional data on these liquids and on the POC-2 liquid[2] are available elsewhere.

The specific gravities of various fractions of the three coal liquids are plotted against the TBP mid-boiling points (T50) of their fractions in Figure 2. The figure shows that the hydrotreated PB3a fractions have lower specific gravities than the corresponding untreated PB3b fractions, due to hydrogen enrichment that occurred during hydrotreating. Figure 2 also shows that the specific gravities of PB3a and POC-2 fractions are almost coincident; both of them were produced using an in-line hydrotreater. Properties of the POC-2 coal liquid, reported elsewhere,[2] are very close to those of PB3a. Different reactor and catalyst types were used for Runs PB-03 (slurry-bed and Fe/Molyvan A) and POC-2 (ebullated-bed and Akzo AO-60); however, the in-line hydrotreater apparently eliminated the effects of differences between reactor and catalyst types in these two runs.

The PB3a total liquid, which was hydrotreated in the HTU, has a higher hydrogen content (12.9 wt %) than the PB3b liquid (11 wt %), which was not hydrotreated. The in-line hydrotreater effectively enriched the liquid product with about 2 wt % of additional hydrogen. The POC-2 coal liquid contains 13.1 wt % of hydrogen, which is close to that of PB3a.

The in-line hydrotreating also reduced dramatically the heteroatom contents of the coal liquid, from 3100 mg/kg sulfur and 6716 mg/kg nitrogen in the untreated PB3b to 600 mg/kg sulfur and 42 mg/kg nitrogen in the hydrotreated coal liquid PB3a. The POC-2 coal liquid contains less sulfur (80 mg/kg) and a similar amount of nitrogen (60 mg/kg). These coal liquids, obtained from a state-of-the-art direct liquefaction process, have an excellent quality.

HYDROGENATION FUNCTION OF THE IN-LINE HYDROTREATER

A closer look at the compositions of the various fractions of these two coal liquid samples reveals clearly that the in-line hydrotreater was very efficient in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). The HDS efficiency on various fractions is in the range of 82-95%, and the HDN efficiency is 99% consistently. The hydrodeoxygenation (HDO) is close to complete. Unsaturated hydrocarbons were effectively saturated during hydrotreating. Figure 3 shows that cycloalkanes were greatly increased, and Figure 4 indicated that aromatics were dramatically reduced in the coal liquid fractions, in accordance with the increase in cycloalkanes. Aromatic hydrocarbons were hydrogenated in the range of 41 to 62%, while olefins were saturated from 74 to 99% for the naphtha fractions. There is an increase, seemingly, in the olefin content of the distillates after hydrotreating. The olefin analysis for heavier fractions, however, is subject to great uncertainty. These results are summarized in Table 4.

The very efficient hydrotreating made the PB3a coal liquid fairly rich in hydrogen and very low in heteroatoms. The in-line hydrotreater removed 80% of the sulfur and 99% of nitrogen and saturated most of the olefins and a substantial part of the aromatics. The PB3a liquid is, therefore, low in aromatics; its gasoline fraction (IBP-177 ^{o}C) contains only 6.5 vol % of aromatics and its diesel fuel fraction (177-288 ^{o}C) contains 32.7 vol % of aromatics. Mild hydrocracking made the coal liquid rich in light materials, mostly in the gasoline boiling range. This is in dramatic contrast with the common perception that coal liquids are highly aromatic, heavy, and viscous.

Overall, the properties of the PB3a coal liquid are similar to those of the POC-2 coal liquid. The lower sulfur content (60 wppm) in the latter may be attributed to the use of supported catalyst in Run POC-2.

CONCLUSIONS

The in-line hydrotreater is highly effective in removing heteroatoms, saturating olefins and aromatics, and boosting gasoline yield in modern direct coal liquefaction. The hydrotreater enriched the coal liquid with 2% hydrogen and provided a mild hydrocracking function, converting a significant amount of the heavier materials into light fractions, mostly in the gasoline range. As a result, the coal liquefaction product that has been processed in the HTU is rich in hydrogen and very low in heteroatoms and aromatics. The hydrotreated coal liquid has a high gasoline yield (38 vol %), which contains very low levels of aromatics (6.5 vol %) and heteroatoms (less than 300 mg/kg sulfur).

The properties of PB3a coal liquid are close to those of the POC-2 coal liquid, which was produced in ebullated-bed reactors with a supported catalyst. The highly effective hydrotreating and mild hydrocracking effects of the in-line hydrotreater eliminated, to a large extent, the effects of differences in reactor and catalyst types. The use of a supported catalyst in Run POC-2 may contribute to the lower sulfur level.

ACKNOWLEDGMENT

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2. Cabbiness, D. “Light Oil Assay of C95029, Syn Products of CONSOL” in DOE/PC 93054-20, “A Characterization and Evaluation of Coal Liquefaction Process Streams, Quarterly Technical Progress Report, June - September, 1995" by G. A. Robbins, S. D. Brandes, R. A. Winschel, and F. P. Burke, December 1995.

Table 1. Operating Conditions for Coal Liquid Samples.

Run	Process Conditions*
PB-03 (sample a)	Catalytic/Catalytic Slurry HTI-Fe/Molyvan A 441 °C/449 °C Criterion C-411/379 °C Distillate Yield 57 wt % MAF coal
PB-03 (sample b)	Catalytic/Catalytic Slurry HTI-Fe/Molyvan A 442 °C/451 °C HTU bypassed Distillate Yield 55 wt % MAF coal
POC-2	Catalytic/Catalytic Ebullated Akzo AO-60 407-414 °C/426-440 °C Criterion C-411/357-382 °C Distillate Yield 62-66 wt % MAF coal

*First-stage/second-stage reactor type
Liquefaction catalyst
First-stage/second-stage reactor temperature
HTU catalyst/temperature
Distillate yield

Table 2. Properties of PB3a Coal Liquid[1]

Fractions, °C	Total Liquid	IBP-21	21-82	82-177	177-204	204-288	288-343	343+
API Gravity	38.0	111.3	65.7	49.8	36.2	27.5	20.9	21.4
Sp. Gr. @15.6 °C	0.8347	0.5830	0.7175	0.7804	0.8437	0.8898	0.9285	0.9254
Elemental, wt %								
Carbon	84.57		84.48	85.92	86.38	87.79	88.65	87.69
Hydrogen	12.92		15.51	14.44	13.17	12.14	12.19	12.29
Sulfur	0.06		<0.01	0.03	0.03	0.02	0.02	0.61
Nitrogen	0.0042		0.0036	0.0023	0.0056	0.0032	0.0019	0.0079
Oxygen (diff)	2.45		0.01	-0.39	0.41	0.05	-0.86	-0.60
Viscosity, cSt								
@ -20 °C					3.832	12.65		
@ 100 °C					0.569	0.952	1.938	3.791
Freezing Pt., °C	-3.9				-60.0	-42		
Smoke Pt., mm					18	11		

Fractions, °C	Total Liquid	IBP-21	21-82	82-177	177-204	204-288	288-343	343+
HC Group, vol %								
Paraffins		98.7	42.98	18.56	13.13	11.52	20.89	
Olefins		0.6	0.33	<0.01	2.40	13.50	23.10	
Naphthenes		0.7	52.54	74.10	60.58	39.10	8.26	
Aromatics		0.0	1.15	7.34	23.89	35.88	47.75	
Benzene			1.03					
Naphthalenes					0.36	5.11		
Thermal Stability (D3241)								
Tube Rating					4.0	>4.0		
Pressure Drop, mmHg					>125	>125		
Oxid. Stability, min			>240	>240	>240			
RON		106	76.1	60.2	54.7			
MON			73.6	58.0	52.1			
Cetane Number					30	32	35	
Net Heat Comb., kJ/kg					42516	41632		

Table 3. Properties of PB3b Coal Liquid[1]

Fractions, °C	Total Liquid	IBP-21	21-82	82-177	177-204	204-288	288-343	343+
API Gravity	24.1	111.3	65.7	43.7	21.2	16.8	12.9	6.4
Sp. Gr. @15.6°C	0.9091	0.5830	0.7175	0.8076	0.9268	0.9540	0.9800	1.0261
Elemental, wt %								
Carbon	83.53		84.39	80.45	81.77	83.85	88.72	88.13
Hydrogen	10.99		15.35	12.74	10.54	10.15	10.58	9.44
Sulfur	0.31		0.19	0.21	0.17	0.12	0.25	0.62
Nitrogen	0.6716		0.3542	0.2005	0.5897	0.8159	0.7197	0.8584
Oxygen (diff)	4.50		-0.28	6.40	6.93	5.06	-0.27	0.95
Viscosity, cSt								
@ -20°C					12.42	73.47		
@ 100°C					0.750	1.199	7.456	7.456
Freezing Pt. °C	too dark				-49	-28		
n-C_7 Ins., wt %	0.09							
Smoke Pt., mm					13	9		
HC Group, vol %								
Paraffins		90.7	42.20	22.15	21.46	13.95	15.57	
Olefins		7.1	7.23	5.01	9.20	4.40	4.40	
Naphthenes		1.9	47.51	55.26	11.83	20.97	5.59	
Aromatics		0.02	3.06	17.58	57.51	60.68	74.44	
Benzene			2.55					
Naphthalenes					6.34	14.92		
Ther. Stability (D3241)								
Tube Rating					4.0	4.0		
Pressure Drop, mmHg					>125	<1.0		
Oxid. Stability, min			>240	>240	>240			
RON		107	75.7	65.6	107			
MON			72.2	66.5	91.2			
Cetane Number					<18.3	<18.3	<18.3	

Fractions, °C	Total Liquid	IBP-21	21-82	82-177	177-204	204-288	288-343	343+
Net Heat Comb., kJ/kg					42145	42219		

Table 4. Hydrogenation Efficiency of the In-Line Hydrotreater

Fraction	% H Increase, absolute	% HDS	% HDN	%HDO	% Olefin Saturation	% Aromatics Saturation
Light Naphtha	0.16	95	99	*	95	62
Medium Naphtha	1.7	86	99	*	99	58
Heavy Naphtha	2.6	82	99	94	74	58
Light Distillate	2.0	83	99	99	**	41
Heavy Distillate	1.6	92	99	*	**	36
Atm. Resid	2.9	2	99	*	n.d.	n.d.

*Negative oxygen by difference prevents calculation
**Higher concentration of olefins determined in hydrotreated product fraction
n.d = not determined

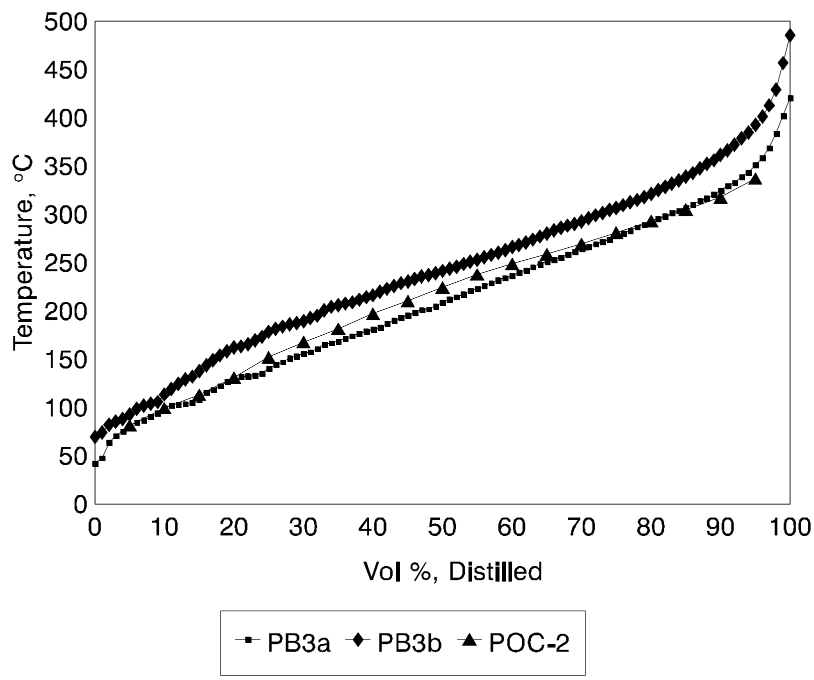

Figure 1. Simulated Distillation Curves of PB3a, PB3b, and POC-2 Coal Liquids.

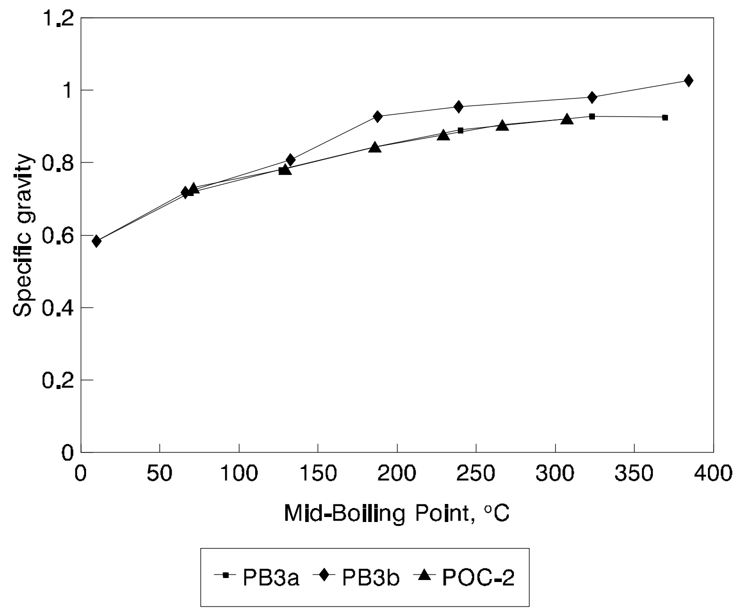

Figure 2. Specific Gravity of PB3a, PB3b, and POC-2 Coal Liquid Fractions.

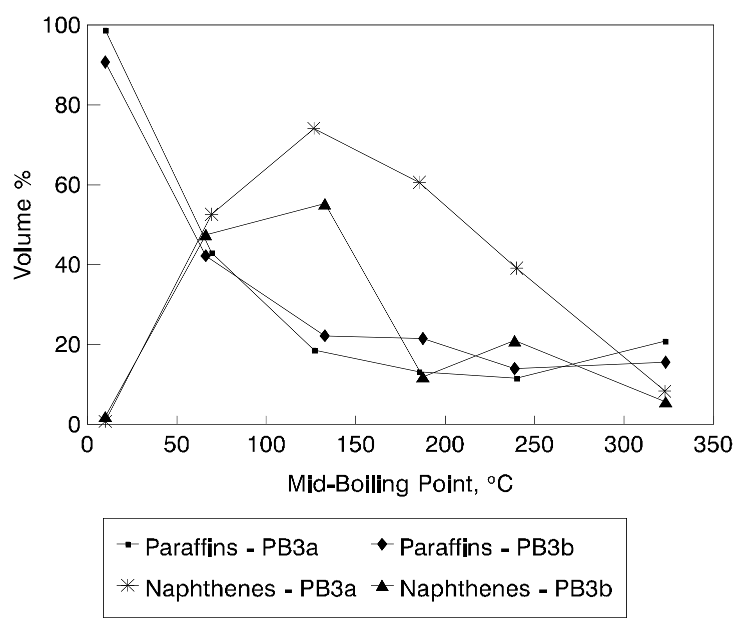

Figure 3. Distribution of Saturated Hydrocarbons in Coal Liquids.

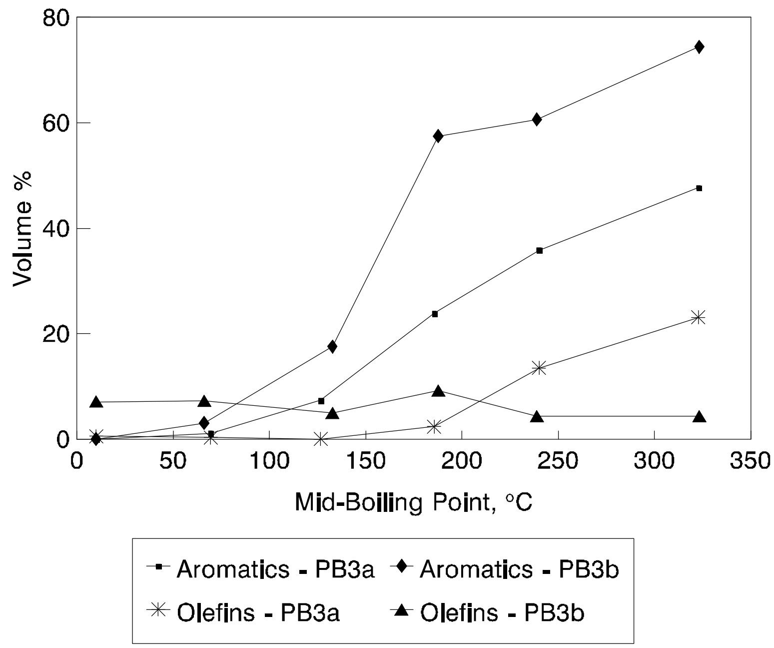

Figure 4. Distribution of Aromatics and Olefins in Coal Liquids.